Quantum Molecular Dynamics Simulations of Liquid Plutonium and Hydrogen/Metal Mixtures

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Warm, dense matter appears in a wide variety of celestial and terrestrial environments—from the interiors of gaseous planets and atmospheres to the plasmas generated by high-energy-density machines and lasers. Other examples include shock-compressed solids and cryogenically cooled liquids, ultracold plasmas, and various stages in primary and secondary nuclear weapons. In general these systems span temperatures from 10^2 K to 10^6 K and beyond, and densities from about 1/100 to 100 the density of a solid. Recently, quantum molecular dynamics (QMD) has been used to accurately predict properties of hydrogen, aluminum, and oxygen-nitrogen mixtures in the warm, dense state. In this report we describe recent work on transport in liquid plutonium and mixtures of metal in hydrogen and metals.

To model such systems, we have applied (QMD) simulation methods that treat the rapidly moving electrons quantum mechanically and the sluggish nuclei classically. In order to provide a systematic representation of the quantum mechanical effects, we have treated the electrons with a state-of-the-art finite-temperature density functional theory (DFT) approach. Specifically, the calculations used the Vienna ab initio Simulation Package with the following common characteristics: a plane-wave basis to represent the wave functions, the generalized gradient approximation density functional, relativistic PAW (projector augmented wave) pseudopotentials without spin-orbit coupling to represent the core electrons. An additional advantage of the QMD methods comes from their integrated nature. Having established the elemental particle interactions, then all the static, dynamical, and optical properties rest on an internally consistent set of principles, whereas in many models of dense media, the representations of these processes arise from different approaches at different levels of approximation.

Plutonium may well be the most complex of elements. At atmospheric pressure, the phase diagram shows six equilibrium solid phases as well as a liquid phase. A study of plutonium introduces another level of complexity because electron spin (magnetic behavior) must also be considered. Although the spin-DFT calculations for the face centered cubic (fcc) lattice structure (δ-Pu) predict an antiferromagnetic (AF) state (in disagreement with the observations of a nonmagnetic state), the predicted structure is quite good, with an atomic volume (V) about 9% less than experiment. We proceeded to study liquid Pu with QMD to explore whether the quantum-derived forces provide a better description than the classical Modified Embedded Atom Method (MEAM) interatomic potential. We worked under the hypothesis that the predicted spin-DFT structural behavior will dominate over the predicted magnetic behavior, especially because the latter should be diminished by the disorder introduced in the liquid structure. An AF-like solution was found for the spin-DFT calculation (net zero magnetic moment with spins allowed to fluctuate on each atom during the MD trajectory). Radial distribution functions were calculated and self-diffusion coefficients (D) were derived from the mean-squared-displacement of the atoms determined from the MD trajectory. In Fig. 1, we compare QMD and classical MD (employing the MEAM potential) calculations of the viscosity of liquid Pu with experimental data. In the classical MD calculations [1], a 1024-atom simulation cell and nonequilibrium (NE) driven-slab boundary conditions were employed to compute the viscosity directly. In the QMD simulations, we calculated the D from the mean-squared-displacement of the atoms determined from an equilibrium MD trajectory with a 54-atom cell; the viscosity (η) was then calculated from a Stokes-Einstein relationship. The MEAM potential was developed to describe the solid phases of Pu, therefore the results from the liquid simulations are a prediction. In this light, the

MEAM values in Fig. 1 are in fair agreement with experiment (within a factor of 5). The preliminary QMD results agree reasonably well with experiment, although we note that a 54-atom simulation is probably too small to provide a definitive answer. Preliminary simulations for 108 atoms (requiring at least 32 Pentium processors in parallel) are yielding results consistent with the result in Fig. 1.

The effect of low to moderate concentrations of titanium metal on the properties of warm, dense hydrogen was studied. The simulations were carried out with a fixed number of particles (either 128 or 512) with a fixed particle density equivalent to a pure hydrogen density of $\rho = 5$ g/cm^3. The titanium concentration Ti was varied form 0 to 16 mol % by replacing more and more hydrogen atoms with titanium atoms. A snapshot from a QMD calculation for 3.9 mol % (Ti) for 512 total particles is shown in Fig. 2. The equation of state (pressure, P) for $\rho = 5$ g/cm^3 as a function of Ti at T = 5 and 10 eV increased quadratically, from P = 11 and 14 TPa, respectively, for Ti = 0 mol %, as Ti was increased up to 16 mol %. As the larger Ti atoms replace the smaller H atoms in the fixed volume, the pressure naturally increases. The self-diffusion coefficient D for hydrogen was also calculated for these conditions. The inverse of D for hydrogen is shown in Fig. 3 for titanium/hydrogen mixtures as a function of Ti. As discussed above, the viscosity η of a liquid is inversely proportional to D, therefore η increases nearly linearly as Ti is increased. As the smaller H atoms are replaced with larger Ti atoms, there is more crowding in the fixed volume, and therefore the resistance to the flow of hydrogen goes up.

[1] F.J. Cherne, M.I. Baskes, and B.L. Holian, *Phys. Rev. B* **67**, 092104 (2003).
[2] E.D. Chisholm and D.C. Wallace, Los Alamos National Laboratory report LA-UR-03-6847 (2003).
[3] L.V. Jones et al., *Trans. Am. Soc. Metals* **55**, 819 (1962).

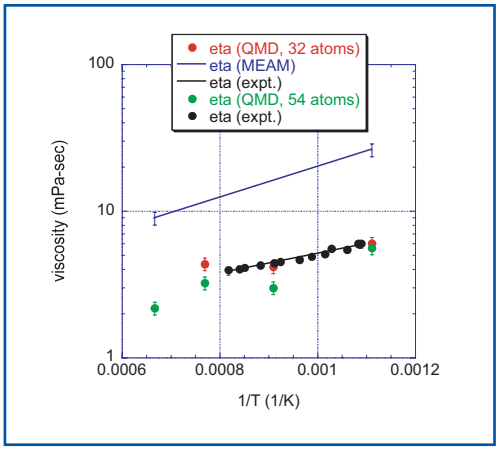

Figure 1— Temperature dependence of plutonium viscosity η. QMD results are for samples of 32 atoms (red circles) and 54 atoms (green circles). Experimental data [3] (black circles).

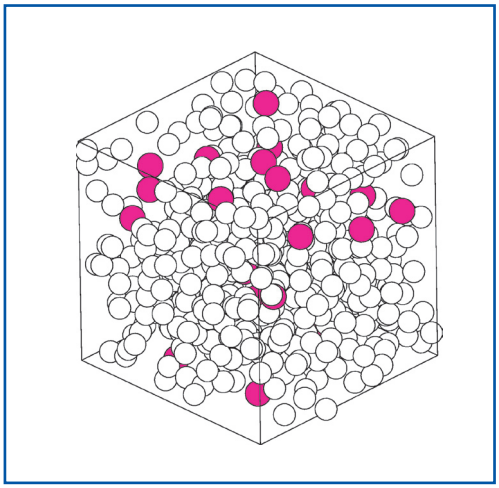

Figure 2— Snapshot from a QMD simulation (512 total atoms) for a 3.9 mol % Ti mixture of hydrogen/titanium.

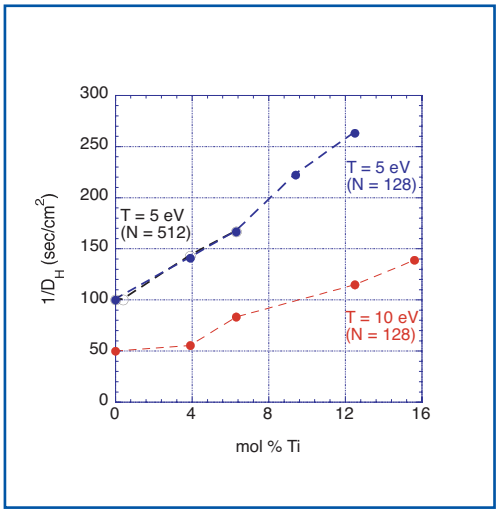

Figure 3— Inverse hydrogen self-diffusion coefficient for hydrogen/titanium mixtures as a function of titanium concentration. Two different temperatures and particle samples (N) are shown for fixed particle density equivalent to 5 g/cm^3 of pure hydrogen.